

## Specific Heats of the Solid-State Phases of Trimargarin and Tristearin

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### ABSTRACT

Differential scanning calorimetry is used to obtain specific heats of the  $\alpha$ ,  $\beta_2'$ ,  $\beta_1'$  and  $\beta$  phases of trimargarin and tristearin in the temperature range from 190-350 K. Unequal specific heats are observed for  $\beta'$  phases of the 2 lipids in contrast to nearly coincident values for their respective  $\alpha$  and  $\beta$  phases. These results are discussed on the basis of odd vs even chain length triglycerides.

### INTRODUCTION

Previous investigations of trimargarin and tristearin have established the existence of 2 intermediate  $\beta'$  phases (1,2). They were conducted to gain information on the contrasting physical properties of even vs odd chain-length monoacid saturated triglycerides. Raman and infrared (IR) spectroscopy, X-ray diffraction and differential scanning calorimetry provide insight into the causes, but do not give total understanding of the even-odd anomaly.

In this study, differential scanning calorimetry (DSC) was used to obtain the specific heats of the 4 phases of trimargarin and tristearin. The behavior of saturated triglyceride solid-state phases are compared.

### MATERIALS AND METHODS

Tristearin and trimargarin were purchased as white crystalline powders from Nu-Chek-Prep, Inc., Elysian, MN, and were used without further purification. Purity was better

than 99% as determined by gas liquid chromatography (GLC).

Specific heat measurements were obtained with a Perkin-Elmer Model DSC-2. The methods followed were fundamentally the same as those described by O'Neill (3) and McNaughton and Mortimer (4). A synthetic sapphire chip was used for calibration. Sample weights ranged from 4.58-13.67 mg. Aluminum cups, covers and sapphire chip were heated at 600 K before each study to achieve and maintain a moisture-free system. Range was 5 mcal/sec. Scanning rate was 20°/min. The temperature range of heat capacity observations from 190 through 350 K was measured in 3 intervals: 185-245 K, 235-295 K and 285-355 K.

Specific phases of tristearin and trimargarin were prepared as in earlier work (1,2). In addition, the  $\beta_1'$  form of trimargarin was obtained by treatment in the DSC as follows. The phase was gradually developed by heating the  $\beta_2'$  phase at 10°/min until initial melting or transition of this phase occurred by the beginning of a sharp endotherm. Heating was halted and isothermal conditions were maintained until equilibrium was again established after a brief exothermal reaction. This procedure was repeated until no subsequent exothermal behavior was apparent.

Each phase was examined for a minimum of 5 runs. Each run consisted of an individually distinct sample, but some samples were used to examine more than one phase.

### RESULTS AND DISCUSSION

Tables I and II contain specific heat values obtained for the

TABLE I

Specific Heats of Trimargarin Phase States<sup>a</sup> (cal/g/°K)

Temperature (°K)	$\beta$ (m.p. = 338) <sup>b</sup>	$\beta_1'$ (m.p. = 335)	$\beta_2'$ (m.p. = 333)	$\alpha$ (m.p. = 323)
340	—	—	—	—
330	0.476 ± 0.016	0.630 ± 0.027	—	—
320	0.434 ± 0.014	0.517 ± 0.012	0.535 ± 0.003	0.617 ± 0.014
310	0.410 ± 0.010	0.463 ± 0.007	0.490 ± 0.002	0.540 ± 0.008
300	0.392 ± 0.010	0.427 ± 0.004	0.456 ± 0.003	0.495 ± 0.007
290	0.377 ± 0.005	0.404 ± 0.005	0.429 ± 0.005	0.470 ± 0.006
280	0.359 ± 0.004	0.386 ± 0.005	0.408 ± 0.006	0.448 ± 0.004
270	0.344 ± 0.005	0.367 ± 0.007	0.387 ± 0.005	0.425 ± 0.002
260	0.330 ± 0.005	0.350 ± 0.006	0.370 ± 0.004	0.404 ± 0.002
250	0.318 ± 0.007	0.333 ± 0.006	0.352 ± 0.004	0.383 ± 0.002
240	0.301 ± 0.004	0.318 ± 0.004	0.335 ± 0.004	0.361 ± 0.004
230	0.288 ± 0.003	0.302 ± 0.003	0.319 ± 0.004	0.341 ± 0.003
220	0.277 ± 0.004	0.288 ± 0.004	0.304 ± 0.005	0.319 ± 0.004
210	0.266 ± 0.005	0.275 ± 0.005	0.291 ± 0.006	0.299 ± 0.004
200	0.254 ± 0.006	0.261 ± 0.004	0.278 ± 0.006	0.282 ± 0.006
190	0.245 ± 0.006	0.251 ± 0.008	0.262 ± 0.006	0.265 ± 0.005

<sup>a</sup>Data are the means and standard deviations of 5 determinations.<sup>b</sup>Melting points are those of reference 2. The values found in this investigation were equal.

TABLE II

Specific Heats of Tristearin Phase States<sup>a</sup> (cal/g/°K)

Temperature (°K)	$\beta$ (m.p. = 345) <sup>b</sup>	$\beta_1'$ (m.p. = 337)	$\beta_2'$ (m.p. = 334)	$\alpha$ (m.p. = 328)
340	—	—	—	—
330	0.455 ± 0.009	0.526 ± 0.006	—	—
320	0.430 ± 0.008	0.476 ± 0.008	0.498 ± 0.012	0.577 ± 0.013
310	0.406 ± 0.009	0.444 ± 0.005	0.463 ± 0.008	0.534 ± 0.015
300	0.385 ± 0.008	0.414 ± 0.004	0.433 ± 0.008	0.490 ± 0.009
290	0.371 ± 0.005	0.392 ± 0.004	0.413 ± 0.006	0.464 ± 0.005
280	0.358 ± 0.006	0.373 ± 0.005	0.392 ± 0.003	0.443 ± 0.007
270	0.344 ± 0.005	0.354 ± 0.003	0.374 ± 0.004	0.420 ± 0.007
260	0.330 ± 0.006	0.338 ± 0.004	0.355 ± 0.005	0.397 ± 0.005
250	0.314 ± 0.007	0.326 ± 0.003	0.335 ± 0.007	0.376 ± 0.006
240	0.301 ± 0.005	0.309 ± 0.002	0.323 ± 0.004	0.354 ± 0.004
230	0.289 ± 0.005	0.297 ± 0.004	0.309 ± 0.002	0.335 ± 0.003
220	0.278 ± 0.006	0.287 ± 0.003	0.296 ± 0.003	0.313 ± 0.006
210	0.266 ± 0.006	0.273 ± 0.002	0.282 ± 0.004	0.292 ± 0.006
200	0.254 ± 0.006	0.260 ± 0.003	0.267 ± 0.003	0.276 ± 0.005
190	0.245 ± 0.007	0.247 ± 0.003	0.252 ± 0.003	0.261 ± 0.003

<sup>a</sup>Data are the means and standard deviations of 5 independent determinations.<sup>b</sup>Melting points are those of reference 1. The values found in this investigation were equal.

$\alpha$ ,  $\beta_2'$ ,  $\beta_1'$  and  $\beta$  phases of trimargarin and tristearin. Charbonnet and Singleton (5) previously reported heat capacities for the  $\alpha$  and  $\beta$  forms of tristearin below 275 K, which agree with those determined here. Recently, tristearin specific heat data for  $\alpha$ ,  $\beta$  and a  $\beta'$  form were reported by Hampson and Rothbart (6) in the temperature range 180–380 K. The specific heat values of  $\alpha$  and  $\beta$  each averaged 0.031 cal/g/deg less than those reported here. Their  $\beta'$  values average 0.029 cal/g/deg less than the tristearin  $\beta_2'$  results reported here and 0.009 cal/g/deg less than the  $\beta_1'$  values. From their method of preparation and because our  $\beta_2'$  values vary as much as the  $\alpha$  and  $\beta$  forms, we concluded that the  $\beta'$  form examined by Hampson and Rothbart was actually the tristearin  $\beta_2'$  phase.

Figure 1 consists of the plots of specific heat values vs temperature for each of the phases in trimargarin and tristearin.

The heat capacity curves exhibit slope discontinuities that have been reported previously (5). Charbonnet and Singleton observed abrupt slope changes for all of the triglycerides they studied (5). The deviations were considerably below the final melting points. For tristearin, their results gave a change in slope of the  $\alpha$  phase at about

230 K and for the  $\beta$  phase at about 258 K. Bailey and Singleton also reported this behavior earlier in a dilatometric investigation of fats (7).

In Figure 1, the tristearin  $\alpha'$  phase shows a perceptible change of slope at 210 K. Following the slope deviation at 210 K, the curve remains straight until 300 K, at which point the curve exhibits a discontinuity by increasing at a much faster rate. The data of Hampson and Rothbart also exhibit the discontinuity at 300 K (6). They also observed the increase in specific heat at 210 K and attributed the change to the reversible sub  $\alpha$ - $\alpha'$  second-order phase transition encountered earlier by Chapman (8), who observed the transition to occur between 223–203 K. The sub  $\alpha$  phase represents a more ordered alkyl chain packing because of reduced chain oscillation at lower temperature. Charbonnet and Singleton showed the slope discontinuity at about 230 K (5). The difference of 20 degrees in the higher temperature of curve deviation is not significant because the temperature of transition is within the limits observed by Chapman. Furthermore, above 208 K, the values of Charbonnet and Singleton are within the boundaries of the standard deviations of our work. This suggests either that their specific heat values at lower temperatures are too high

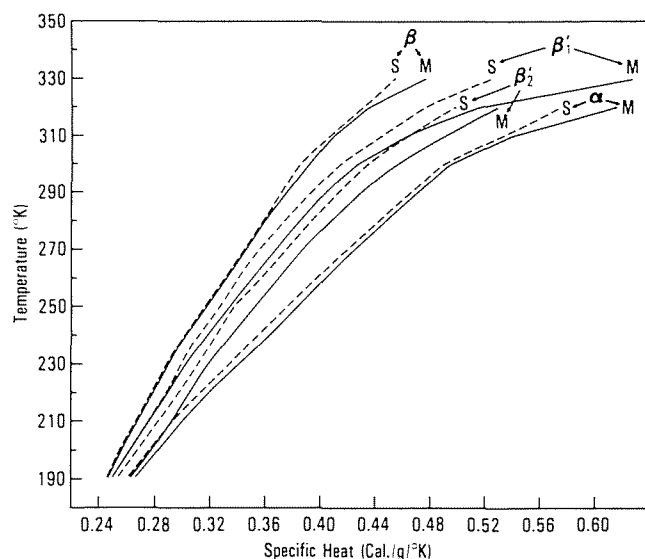


FIG. 1. Comparison of the specific heat plots of trimargarin (M) and tristearin (S) phases. Trimargarin is represented by the solid curve and tristearin by the dashed curve.

or that the true sub  $\alpha$ - $\alpha$  transition temperature is hidden by analysis error in the 210-230 K range.

$\beta$ -Tristearin shows a similar discontinuity at ca. 250 K, which agrees with Charbonnet and Singleton (5). The data of Hampson and Rothbart are too irregular in this temperature range to draw any conclusions (6). The  $\beta$  phase data are not precise enough to determine if the curve immediately above the change at 250 K is straight or slightly curved. Analogous to the  $\alpha$  phase, the  $\beta$  form heat capacity reveals a second discontinuity above 300 K where the heat capacity increases much more rapidly, an effect also observed in the results of Hampson and Rothbart (6). The tristearin  $\beta_2'$  phase exhibits the same trend as the  $\alpha$  and  $\beta$  forms with slope deviations at 250 and 300 K. The precise location of  $\beta_1'$  deviations is somewhat more complex and will require additional data.

With trimargarin, similar observations hold. Discontinuities occur at 210 K and 300 K for the  $\alpha$  form. However, the remaining 3 phases possessed definite heat capacity discontinuities only at 300 K for  $\beta_1'$  and at 310 K for the  $\beta$  phase.

Charbonnet and Singleton viewed the higher temperature discontinuity as an indication of premelting (5). Brinkman, Fisher and Moncton (9) have extended a concept of 2-dimensional melting, first put forth by Kosterlitz and Thouless (10), and applied it to liquid crystals and lipids. Such systems consists of films 1-2 molecules thick. Their concept is applicable here because the crystalline domains of triglycerides are layered structures in which intralayer packing is determined by lateral alkyl chain interactions that are, in toto, much stronger than the interactions that occur between layers at ends of the alkyl chains. Within the lateral structure exist defects, e.g., as molecular or alkyl chain dislocations. With heating, the order of the 2 dimensional system is gradually destroyed as the defect areas increase in energy and size. As the temperature increases, the defects grow, creating liquid like domains that destroy the lattice.

Figure 1 relates the specific heat curves of the tristearin phases to those of trimargarin. The 2  $\beta$ -phase curves are nearly coincident. Examination of the 2  $\alpha$ -phase curves shows they are parallel and virtually coincident except above 310 K. At this point, the  $\alpha$  phases of the 2 triglycerides approach their transition temperatures at different rates. The cause of this anomaly is not known.

Similar  $\alpha$  and  $\beta$  heat capacities for these 2 triglycerides were expected. Values of the even-membered triglyceride heat capacities determined by Charbonnet and Singleton for the  $\alpha$  and  $\beta$  phases from trilaurin through tristearin are nearly equal for any given temperature (5). Although no heat capacities of odd-membered triglycerides are given in the literature, the heat capacities of even- and odd-saturated alkanes from n-dodecane through n-octadecane exhibit the same constancy in heat capacities (11). We assume, therefore, that the heat capacity values for trimargarin exemplify those for odd chain-length triglycerides,  $C_{15}$  through  $C_{23}$ , and that tristearin does that same for even chain-length triglycerides,  $C_{16}$  through  $C_{24}$ . These ranges are derived from the observation of Hagemann and Rothfus (12) that each triglyceride exhibited 2  $\beta'$  phases.

In contrast to the nearly equal heat capacities for the corresponding  $\alpha$  and  $\beta$  phases of tristearin and trimargarin, the heat capacities of  $\beta_1'$  and  $\beta_2'$  of tristearin do not coincide with the respective  $\beta'$  heat capacities of trimargarin. Figure 1 reveals that the even and odd  $\beta'$  phase specific heat curves are distinctly different from each other. Similarity and dissimilarity between trimargarin and tristearin provide an interesting comparison with other physical properties that alternate with even and odd chain length, e.g., melting points and angles of tilt of the hydrocarbon chain axes.

Melting points of triglyceride phases have been provided by Hagemann and Rothfus (12). The  $\alpha$ -phase melting points of even and odd triglycerides form a continuous smooth curve. In contrast,  $\beta$ -phase melting points of these molecules alternate between even- and odd-membered chain lengths, the even being higher than the odd. Hagemann Rothfus (12) show that the  $\beta'$  phases also form a curve of alternating melting points, although the severity of alternation is much less than that of the  $\beta$  phase series.

Long spacings of the crystalline unit cells are measures of the chain tilt of the hydrocarbon portion of the triglyceride. If the long spacings of the even- and odd-membered chain-length triglycerides,  $C_{11}$  through  $C_{18}$ , are plotted vs chain length, the following observations are made (8). The  $\alpha$  phase long spacings all fall on a linear line. For  $\beta'$  phase long spacings, the line through points for even-membered triglycerides lies above that for odd-membered triglycerides, i.e., an alternation exists between the 2 species for this physical trait. A similar but opposite alternation occurs for the  $\beta$  phase. The odd-membered chain-length species possesses relatively greater long spacings than even-membered triglycerides.

As expected, no irregularity in the physical properties of the  $\alpha$  phases occurred. Both odd and even long chain-length lipids are known to pack hexagonally with chain oscillation (13,14). The  $\beta$  phase heat capacities of the odd and even triglycerides, trimargarin and tristearin, are equal. Respective  $\beta'$  heat capacities do differ significantly. This contrast of congruent  $\beta$  phase heat capacities against unequal  $\beta'$  heat capacities is important. In previous comparisons of odd vs even triglyceride physical properties, the  $\beta$  phase has exhibited alternation. The anomaly observed here lacks an immediate explanation.

When the heat capacity curves for the  $\beta'$  states of trimargarin and tristearin are extrapolated to higher temperatures than those in Figure 1, the following observations result. The heat capacity values of the  $\beta'$  phases of trimargarin cross at ca. 322 K, 11 degrees below the  $\beta_2'$  melting point. Extrapolations of curves of the  $\beta'$  phases of tristearin converge at ca. 337 K, the melting temperature of the  $\beta_1'$  state and higher than the  $\beta_2'$  melting point. These extrapolations show that only trimargarin attains a temperature below either  $\beta'$  melting point at which the structural ener-

gies of both  $\beta'$  states appear to be equal. Whether the 2  $\beta$  phases possess nearly identical solid-state structures at the crossover temperature cannot be determined from our data. Such a conclusion requires determination of molecular volumes, coefficients of expansion, and the energy of the  $\beta_2'$  to  $\beta_1'$  phase transition.

These results on individual solid phases of monoacid triglycerides reinforce evidence that even and odd chain-length saturated triglycerides exhibit distinctly different polymorphic behavior. An explanation of the  $\beta'$  specific heat anomaly observed in this work might also identify reasons for the alternation of physical properties between the  $\beta'$  states of even- and odd-membered triglycerides.

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#### REFERENCES

1. Simpson, T.D., and J.W. Hagemann, *JAOCS* 59:169 (1982).
2. Simpson, T.D., *JAOCS* 60:19 (1983).
3. O'Neill, M.J., *Anal. Chem.* 38:1331 (1966).
4. McNaughton, J.L., and C.T. Mortimer, *Int. Rev. Sci.: Phys. Chem.*, Ser. Two 10:1 (1975).
5. Charbonnet, G.H., and W.S. Singleton, *JAOCS* 24:140 (1947).
6. Hampson, J.W., and H.L. Rothbart, *Ibid.* 60:1102 (1983).
7. Bailey, A.E., and W.S. Singleton, *Oil & Soap* 22:265 (1945).
8. Chapman, D., *Chem. Rev.* 62:433 (1962).
9. Brinkman, W.F., D.S. Fisher and D.E. Moncton, *Science* 217:693 (1982).
10. Kosterlitz, J.M., and D.J. Thouless, *J. Phys. C* 6:1181 (1973).
11. Passut, C.A., and R.P. Danner, *Ind. Eng. Chem. Process Des. Dev.* 11:543 (1972).
12. Hagemann, J.W., and J.A. Rothfus, *JAOCS* 60:1123 (1983).
13. Larsson, K., *Arkiv Kemi* 23:35 (1965).
14. Hernqvist, L. and K. Larsson, *Fette Seifen Anstrichm.* 84:349 (1982).

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